HERMES DECLARATION
EXHIBIT 15 – PART 2 OF 8

US005314446A

United States Patent [19]

Hunter et al.

[11] Patent Number: 5,314,446

[45] Date of Patent: May 24, 1994

[54] STERILIZED HETEROGENEOUS BRAIDS

[75] Inventors: Alastair W. Hunter, Bridgewater; Arthur Taylor, Jr., Plainfield, both of N.J.; Mark Steckel, Maineville, Ohio

[73] Assignee: Ethicon, Inc., Somerville, N.J.

[21] Appl. No.: 838,511

[22] Filed: Feb. 19, 1992

[51] Int. Cl.[5] D04C 1/00

[52] U.S. Cl. 606/231; 606/228; 87/7; 87/9; 428/370

[58] Field of Search 606/228, 230, 231; 87/7, 8, 9; 428/225

[56] References Cited

U.S. PATENT DOCUMENTS

3,187,752	6/1965	Glick	128/335.5
3,463,158	8/1969	Schmitt et al.	606/228
3,527,650	9/1970	Block	117/7
3,636,956	1/1972	Schneider	128/335.5
3,942,532	3/1976	Hunter et al.	128/335.5
4,043,344	8/1977	Landi et al.	128/335.5
4,047,533	8/1977	Perciaccante et al.	128/335.5
4,052,988	10/1977	Doddi et al.	128/335.5
4,141,087	2/1979	Shalaby et al.	3/1
4,470,941	9/1984	Kurtz	264/136
4,624,256	11/1986	Messier et al.	128/335.5
4,946,467	8/1990	Ohi et al.	606/228
4,959,069	9/1990	Brennan et al.	606/228
4,979,956	12/1990	Silverstrini	623/13
5,116,360	5/1992	Pinchuk et al.	623/1
5,147,400	9/1992	Kaplan et al.	623/13

FOREIGN PATENT DOCUMENTS

2949920	3/1981	Fed. Rep. of Germany	A61F 1/00
WO86/00020	1/1986	PCT Int'l Appl.	A61L 17/00
2082213	8/1980	United Kingdom .	
2218312A	11/1989	United Kingdom	A01K 91/00

Primary Examiner—George F. Lesmes
Assistant Examiner—Chris Raimund
Attorney, Agent, or Firm—Hal Brent Woodrow

[57] ABSTRACT

Heterogeneous braided multifilament of first and second set of yarns mechanically blended by braiding, in which first and second set of yarns are composed of different fiber-forming materials.

Heterogeneous braids are useful for preparation of surgical sutures and ligatures.

12 Claims, 3 Drawing Sheets

FIG-1

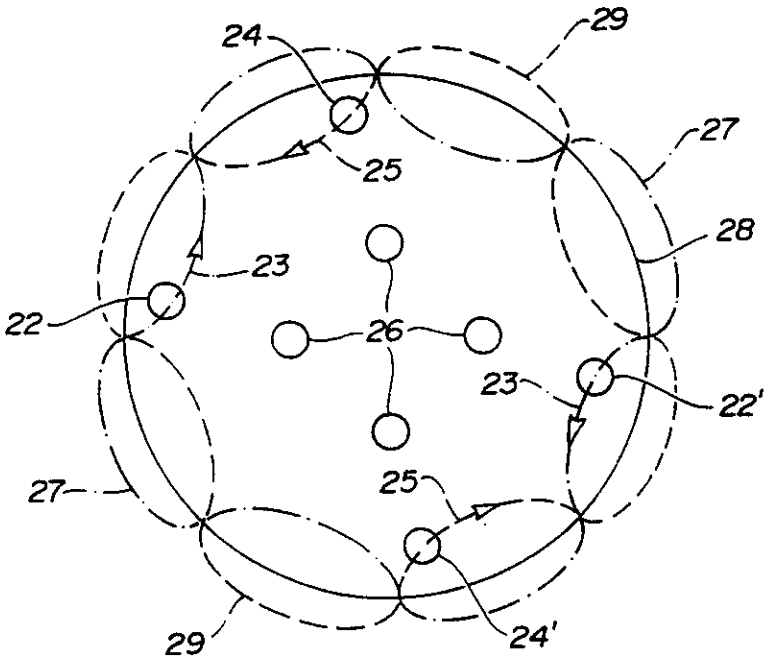


FIG-2

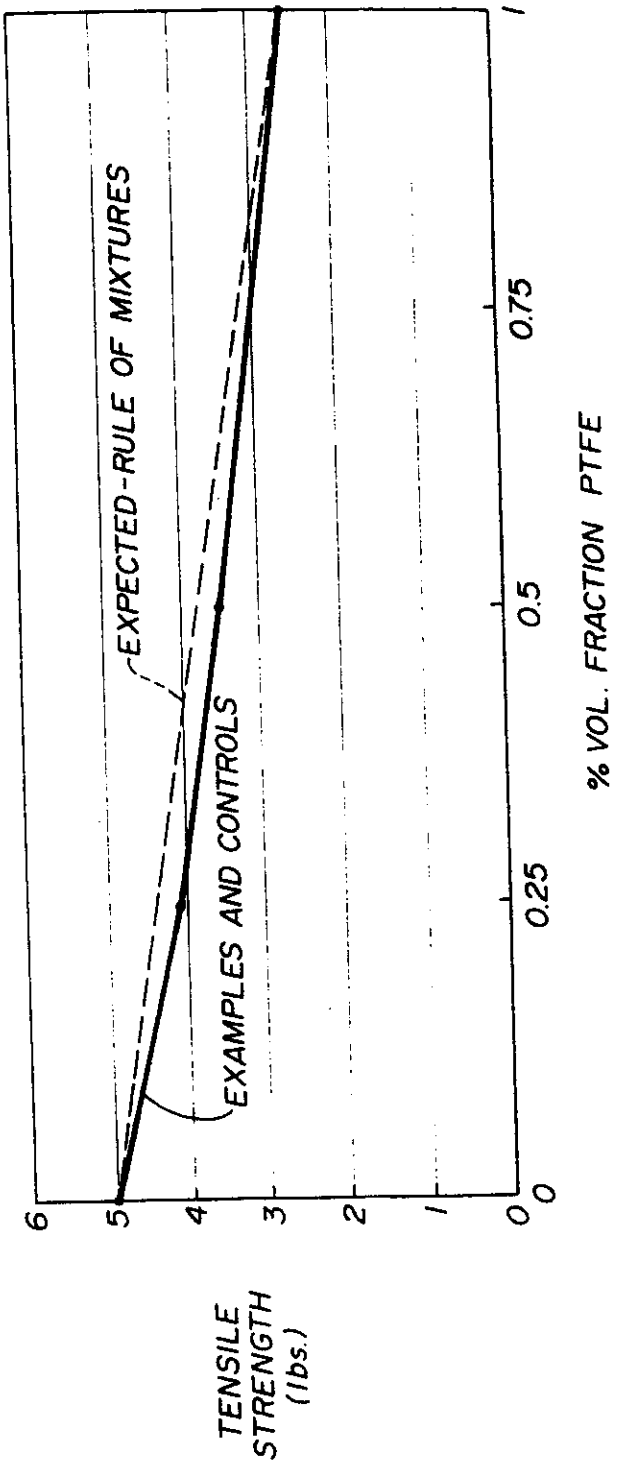
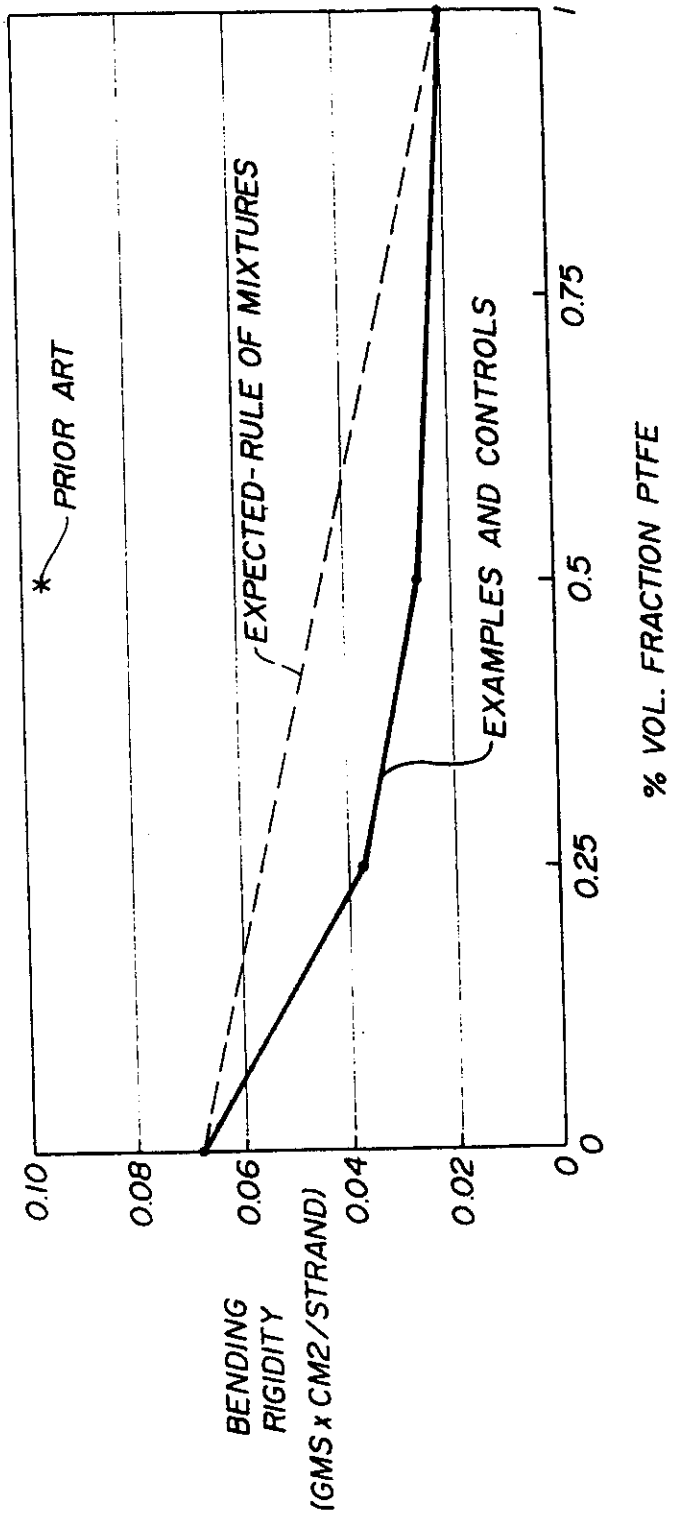

EXPECTED-RULE OF MIXTURES
EXAMPLES AND CONTROLS
TENSILE STRENGTH (lbs.)
6
5
4
3
2
1
0
0
0.25
0.5
0.75
1
% VOL. FRACTION PTFE

FIG-3


PRIOR ART
EXPECTED-RULE OF MIXTURES
EXAMPLES AND CONTROLS
0.10
0.08
0.06
0.04
0.02
0
0.25
0.5
0.75
1
BENDING RIGIDITY (GMS x CM2/STRAND)
% VOL. FRACTION PTFE

STERILIZED HETEROGENEOUS BRAIDS

BACKGROUND OF THE INVENTION

This invention relates to braided multifilaments, and especially to sterilized, braided multifilaments suitably adapted for use as surgical sutures or ligatures.

Braided multifilaments often offer a combination of enhanced pliability, knot security and tensile strength when compared to their monofilament counterparts. The enhanced pliability of a braided multifilament is a direct consequence of the lower resistance to bending of a bundle of very fine filaments relative to one large diameter monofilament. However, for this enhancement to be realized, the individual multifilaments must be able to bend unencumbered or unrestricted by their neighboring filaments. Any mechanism which reduces this individual fiber mobility, such as simple fiber-fiber friction, a coating which penetrates into the braid interstices, or a melted polymer matrix which adheres fibers together, will adversely affect braid pliability. In the extreme case where the multifilaments are entirely bonded together, the pliability or bending resistance closely approximates that of a monofilament.

Unfortunately, the prior art abounds with attempts to improve specific properties of multifilament braids at the expense of restricting the movement of adjacent filaments which make up the braid,. For example, multifilament sutures almost universally possess a surface coating to improve handling properties.

U.S. Pat. No. 3,942,532 discloses a polyester coating for multifilament sutures. The preferred polyester coating is polybutilate, which is the condensation product of 1,4-butanediol and adipic acid. U.S. Pat. No. 4,624,256 discloses a suture coating copolymer of at least 90 percent ϵ-caprolactone and a biodegradable monomer, and optionally a lubricating agent. Examples of monomers for biodegradable polymers disclosed include glycolic acid and glycolide, as well as other well known monomers typically used to prepare bioabsorbable coatings for multifilament sutures.

An alternative to the use of the commonly accepted coating compositions for multifilament sutures to improve handling properties is disclosed in U.S. Pat. 3,527,650. This patent discloses a coating composition of polytetrafluoroethylene (PTFE) particles in an acrylic latex. Although the PTFE particles act as an excellent lubricant to decrease the surface roughness of multifilament sutures, the particles have a tendency to flake off during use. Also, this particular coating is a thermoset which requires a curing step for proper application.

More recently, a dramatic attempt has been made to create a monofilament-like surface for a multifilament suture. U.S. Pat. No. 4,470,941 discloses the preparation of "composite" sutures derived from different synthetic polymers. The composite suture is composed of a core of low melting fibers around which are braided high melting fibers. Because of the lack of cohesiveness of the dissimilar fibers, the low melting fibers in the core are melted and redistributed throughout the matrix of the braided, high melting fibers. Although these composite sutures represent an attempt to combine the best properties of different synthetic fibers, it unfortunately fails in this respect due to increased stiffness (as evidenced by FIG. 3 which is described in detail below), apparently due to the reduction of fiber mobility resulting from the fusing of the fibers together.

Another attempt to enhance the properties of multifilament sutures can be found in WO 86/00020. This application discloses coating an elongated core of a synthetic polymer having a knot tenacity of at least 7 grams/denier with a film-forming surgical material. The film-forming surgical material can be absorbable or nonabsorbable, and can be coated on the elongated core by solution casting, melt coating or extrusion coating. Such coated multifilament sutures suffer from the same deficiencies which plague conventionally coated multifilament sutures.

All of the attempts described in the prior art to improve braid properties have overlooked the importance of fiber-fiber friction and its impact on fiber mobility and braid pliability. The properties of concern here include the fiber-fiber frictional coefficients (which frequently relate to the polymer's surface energy), the fiber cross-sectional shape and diameter, and the braid structure which influences the transverse forces across the braid. If fibers composed of highly lubricous polymers are used in the traditional manner, then a highly pliable braid can be prepared. However, in most cases, these braids will be relatively weak and unusable. Hence, a tradeoff between braid strength and pliability exists in the design of conventional braided multifilaments.

In view of the deficiencies of the prior art, it would be desirable to prepare multifilament sutures exhibiting improved pliability and handling properties. More specifically, it would be most desirable to prepare braided multifilaments composed of dissimilar fiber-forming materials in which the fiber-forming materials contribute significantly to enhanced pliability for the braided multifilament without appreciably sacrificing its physical properties.

SUMMARY OF THE INVENTION

The invention is a heterogeneous braid comprising a first and second set of continuous and discrete yarns in a sterilized, braided construction. At least one yarn from the first set is in direct intertwining contact with a yarn from the second set.

Each yarn from the first set is composed of a plurality of filaments of a first fiber-forming material, and each yarn from the second set is composed of a plurality of filaments of a second fiber-forming material.

Surprisingly, the heterogeneous braids may exhibit a combination of outstanding properties attributable to the specific properties of the dissimilar fiber-forming materials which make up the braided yarns. The dissimilar fiber forming materials do not require melt bonding or any other special processing techniques to prepare the heterogeneous braids of this invention. Instead, the integrity of the braid and therefore its properties is due entirely to the mechanical interlocking or weaving of the individual yarns. In fact, it is possible to tailor the physical and biological properties of the braid by varying the type and proportion of each of the dissimilar fiber forming materials used, as well as adjusting the specific configuration of the braid. For example, in preferred embodiments, the heterogeneous braid will exhibit improved pliability and handling properties relative to that of conventional homogeneous fiber braids, without sacrificing physical strength or knot security.

The sterilized, heterogeneous braids of this invention are useful as surgical sutures or ligatures, as well as for

the preparation of any other medical device which would benefit from its outstanding physical or biological properties.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a carrier layout for the preparation of a heterogeneous braid within the scope of this invention;

FIG. 2 is a plot representing the relationship between the tensile strength of heterogeneous and homogeneous braids of polyethylene terephthalate (PET) and PTFE yarns, and the volume fraction of PTFE yarns in the braids; and

FIG. 3 is a plot representing a relationship between the initial bending rigidity of heterogeneous and homogeneous braids of PET and PTFE yarns, and the volume fraction of PTFE yarns in the braids.

DETAILED DESCRIPTION OF THE INVENTION

For purposes of describing this invention, a "heterogeneous" braid is a configuration composed of at least two sets of dissimilar yarns mechanically blended by intertwining the dissimilar yarns in a braided construction. The yarns are continuous and discrete, so therefore each yarn extends substantially along the entire length of the braid and maintains its individual integrity during braid preparation, processing and use.

The heterogeneous braids of this invention can be conventionally braided in a tubular sheath around a core of longitudinally extending yarns, although such a core may be excluded, if desired. Braided sheath sutures with central cores are shown in U.S. Pat. Nos. 3,187,752; 4,043,344; and 4.047,533, for example. A core may be advantageous because it can provide resistance to flattening, as well as increased strength. Alternatively, the braids of this invention can be woven in a spiral or spiroid braid, or a lattice braid, as described in U.S. Pat. Nos. 4.959,069 and 5,059,213.

The dissimilar yarns of the first and second set of yarns are braided in such a manner that at least one yarn from the first set is directly intertwined with, or entangled about, a yarn from the second set. Direct mechanical blending of individual, dissimilar yarns therefore occurs from the interweaving and interlocking of these dissimilar yarns, enhancing yarn compatibility and the overall physical and biological properties of the heterogeneous braid. Preferably, every yarn from the first set is in direct intertwining contact with a yarn of the second set to achieve the maximum degree of mechanical blending of the dissimilar yarns.

The first and second fiber-forming materials which make up the filaments of the first and second set of yarns, respectively, can be any materials capable of being spun into continuous filaments. Advantageously, the fiber-forming materials are nonmetallic.

The preferred fiber-forming materials are synthetic fiber-forming polymers which are melt or solution spun through a spinneret to prepare continuous filaments. The filaments so prepared are advantageously stretched to provide molecular orientation and annealed to enhance dimensional stability and/or biological performance. The fiber-forming polymers can be bioabsorbable or nonabsorbable, depending on the particular application desired. Examples of monomers from which bioabsorbable polymers are derived include, but are not limited to, some hydroxyacids and lactones, e.g. glycolic acid, lactic acid, glycolide, lactide, p-dioxanone, ε-caprolactone and trimethylene carbonate, as well as copolymers and polymer blends derived from these monomers and others. Interestingly, numerous bioabsorbable heterogeneous braids exhibiting varying useful biological properties, such as breaking strength retention in vivo and the absorption profiles in vivo, can be prepared for specific applications by using different combinations of bioabsorbable polymers.

Preferably, the continuous filaments which make up the first and second set of yarns are derived from nonabsorbable polymers. In a preferred embodiment, the first set of yarns acts as lubricating yarns to improve the overall pliability, or compliance, and surface lubricity of the heterogeneous braid. Preferably, the fiber-forming material of the first set exhibits a surface energy (which frequently relates to surface lubricity) less than about 38 dyne/cm, as measured by contact angle of liquids on polymer surfaces, as described by Kissa, E., "Handbook of Fiber Science and Technology," Vol. II, Part B, Marcel Decker, 1984. Such fiber forming polymers include perfluorinated polymers, e.g. PTFE and fluorinated ethylene/propylene copolymers (FEP) and perfluoroalkoxy (PFA) polymers, as well as non-perfluorinated polymers such as polyvinylidene fluoride (PVDF), polyethylene/tetrafluorethylene copolymers (PETFE), the polycholorofluoroethylene polymers, polypropylene (PP) and polyethylene (PE). More preferably, the first fiber-forming material exhibits a surface energy less than about 30 dyne/cm. The preferred polymers for the first set are PTFE, PETFE, FEP, PE and PP, and the most preferred fiber forming polymer is PTFE.

In a more preferred embodiment, the lubricating yarns of the first set are mechanically blended with yarns of the second set which act to provide improved strength to the heterogeneous braid. Preferably, the second set of yarns exhibits a yarn tenacity greater than 3.0 grams/denier, more preferably greater than 5.0 grams denier. The preferred yarns are PET, nylon and aramid, and the most preferred yarns are PET.

In the most preferred embodiment, the heterogeneous braid is composed of a first set of PTFE yarns mechanically blended with a second set of PET yarns in a braided configuration. Advantageously, the braided sheath encloses a core of longitudinally extending PET yarns to further improve the overall strength and resistance to flattening of the heterogeneous braid. In this embodiment, the volume fraction of lubricating yarns in the braided sheath and core desirably ranges from about 20 to about 80 percent. A volume fraction of lubricating yarns below about 20 percent will not typically improve the pliability of the braid, and a volume fraction above about 80 percent may adversely affect the overall strength of the braid. The filament fineness for such a heterogeneous braid is preferably less than 10 denier per filament, preferably from about 0.5 to about 5 denier per filament. A more coarse filament may result in a stiffer braid. The preferred individual yarn denier is between 10 and 100 denier.

The heterogeneous braids of this invention can be prepared using conventional braiding technology and equipment commonly used in the textile industry, and in the medical industry for preparing multifilament sutures. For example, the first and second set of yarns can be interwoven as indicated by the plan view of the yarn carrier layout of FIG. 1 for the preparation of a braided multifilament. The individual yarns of the braided sheath feed from spools mounted on carriers 22, 22' and

CONTROL I

FIBER MATERIALS: An 8×0 PET braid is fabricated, i.e. 8 sheath yarns and 0 core yarns. All yarns are Dupont Dacron PET, 70 denier, 48 filament, type 52 yarn.

PROCESSING: The yarns are wound on braider bobbins per conventional methods, and the bobbins loaded on each carrier of a N.E. Butt 8 carrier braider. Machine settings include: 32 pick gear, 0.009" wire tension springs, and 183 rpm. The braid is aqueous scoured, and hot stretched at 30% draw ratio at 225° C.

CONTROL II

FIBER MATERIALS: An 8×0 PTFE braid is fabricated. All yarns are Dupont Teflon, 110 denier, 12 filament.

PROCESSING: The yarns are wound on braider bobbins per conventional methods, and the bobbins loaded on each carrier of a N.E. Butt 8 carrier braider. Machine settings include: 36 pick gear, no tension springs, and 183 rpm. The braid is scoured and hot stretched per the conditions described in CONTROL I.

EXAMPLE I

FIBER MATERIALS: An 8×0 heterogeneous braid is fabricated, consisting of four PET 70 denier yarns and four PTFE 110 denier yarns. The yarns are identical to that employed in CONTROL I and II. On a volume basis, the braid is 50.3% PET, and 49.7% PTFE.

PROCESSING: Four bobbins of PET yarn and four bobbins of PTFE yarn were wound by conventional means. The PET bobbins were loaded on the clockwise moving carriers of the N.E. Butt 8 carrier braider, and the PTFE yarn bobbins on the counter-clockwise moving carriers. Machine settings include: 32 pick gear, 0.009" tension springs on PET carriers, no springs on PTFE carriers, and 183 rpm. The braid is scoured and hot stretched per the conditions described in CONTROL I.

EXAMPLE II

FIBER MATERIALS: Identical to EXAMPLE I, except that 6 PET yarns and 2 PTFE yarns were used. On a volume basis, the braid is 75.5% PET, and 24.5% PTFE.

PROCESSING: Identical to EXAMPLE I, except that 2 PET bobbins replace 2 PTFE bobbins. All other braider machine settings, scour and hot-stretch conditions are identical to CONTROL I and II and EXAMPLE I.

PRIOR ART I

FIBER MATERIALS: Identical to EXAMPLE I. On a volume basis, the braid is 50.3% PET, and 49.7% PTFE.

PROCESSING: Identical to EXAMPLE I, except that the hot stretch temperature is at 300° C. and for a longer residence time to facilitate melting of the PET fibers.

The properties of CONTROLS I and II, and EXAMPLES I and II, and the PRIOR ART I are summarized in the following Table:

	USP DIAMETER (mils)	TENSILE STRENGTH (lbs)	KNOT STRENGTH (lbs)	BENDING RIGIDITY (gm × cm²)	KNOT STABILITY (# of throws)
CONTROL I	10.68	4.98	3.14	0.0680	4
CONTROL II	9.11	2.58	2.04	0.0196	7
EXAMPLE I	9.71	3.55	2.41	0.0257	5
EXAMPLE II	10.35	4.10	2.67	0.0371	5
PRIOR ART I	8.81			0.0966	

As may be expected, the tensile strengths of the heterogenous braid examples reflect the relative contributions of the individual components. This behavior is said to follow the "rule of mixtures", i.e. the composite property is a weighted average of the component properties. In equation form,

$$P_c = (Vf_a)(P_a) + (Vf_b)(P_b)$$

where P_c is a composite property (such as tensile strength or modulus), P_a and P_b are the properties of the components a and b, and Vf_a and Vf_b are the volume fractions of components a and b. This behavior is clearly observed in FIG. 2, which shows a plot of tensile strength versus volume fraction of PTFE yarns for the Examples and Controls, in relation to the expected plot according to the rule of mixtures.

Surprisingly, the bending rigidity of the heterogeneous braids in EXAMPLES I and II do not follow the rule of mixtures, and show an enhanced bending rigidity relative to the weighted average of its components. This is shown in FIG. 3 as a plot of bending rigidity versus %PTFE in the braids. Bending rigidity is the inverse of pliability, and is obtained by measuring the slope of the *bending moment-radius of curvature* plot of a suture strand in pure bending. Hence lower bending rigidity relates to a more pliable suture, which is a highly desirable property. The mechanism of this enhanced pliability is believed to be internal lubrication of the braid by the "solid lubricant" behavior of the low surface energy PTFE.

U.S. Pat. No. 4,470,941 discloses the preparation of a "composite" suture with a monofilament-like surface made from multifilament yarns. The composite suture is composed of two different synthetic polymer fibers, which is thermally processed to melt one of the fibers to form a continuous matrix. This process was utilized to produce the PRIOR ART I example, the data of which is shown in Table 1 and FIG. 3. It is observed that the melting of the PET fibers significantly increases the braid bending rigidity due to the bonding of the "non-melted" fibers together, hence resulting in a less pliable braid of diminished utility.

What is claimed is:

1. A surgical suture consisting essentially of a heterogeneous braid composed of a first and second set of continuous and discrete yarns in a sterilized, braided construction wherein at least one yarn from the first set is in direct intertwining contact with a yarn from the second set; and

24, 24'. The carriers move around the closed circular loop 28, moving alternately inside and outside the loop 28 to form the braiding pattern. One or more carriers are continually following a serpentine path in a first direction around the loop, while the remaining carriers are following a serpentine path in the other direction.

In the illustrated embodiment, carriers 22, 22' are travelling around serpentine path 27 in a clockwise direction as indicated by directional arrows 23, and carriers 24, 24' are travelling around serpentine path 29 in a counterclockwise direction as indicated by arrows 25. The moving carriers dispense yarns which intertwine to form the braid. The yarns from all the carriers in a constructed embodiment of FIG. 1 are dispensed upward with respect to the plane of the drawing, and the braid is taken up on a reel located above the plane of the drawing.

In one embodiment, moving carriers 22, 24 dispense yarns of the first set and moving carriers 22', 24' dispense yarns of the second set to form the heterogeneous braid. In a more preferred embodiment, moving carriers 22, 22' dispense yarns of the first set and moving carriers 24, 24' dispense yarns of the second set. This carrier layout provides a braid in which each yarn of the first set is directly intertwined with a yarn from the second set.

Advantageously, as illustrated in FIG. 1, disposed within the center of the loop 28 are carriers 26 which dispense the core yarns of the braid. In the most preferred embodiment of this invention. moving carriers 22, 22' dispense PTFE yarns, moving carriers 24, 24' dispense PET yarns, and core carriers 26 dispense PET yarns.

Numerous additional embodiments are contemplated within the scope of the invention using conventional braiding technology and equipment. For example, the carrier layout can be modified to prepare a braid configuration using from 3 to 28 sheath carriers, with or without any number of core yarns. Dissimilar yarns from the first and second set of yarns can be plied together using conventional techniques before braiding, and in this embodiment, the carriers can dispense identical bobbins of plied yarns composed of individual yarns from the first and second sets. This embodiment not only offers the advantage of inter-yarn mechanical blending, but also the intimate mixing associated with intra-yarn blending.

Similar to the preparation of conventional homogeneous braids, the yarns from which the heterogeneous braids are prepared are preferably nontextured. The yarn tension during braiding is advantageously adjusted so that the yarn elongation for each set of yarns is about equal. The equilibration of yarn elongation may prevent irregularities, for example. "core popping", which is the tendency of core yarns to break through the braided sheath as the braid is bent. The number of picks per inch in the finished braid can be adjusted to balance the tensile strength of the braid with braid quality, e.g. the tendency for core popping and overall braid smoothness.

After the heterogeneous braid is prepared, it is desirably scoured to remove machine oils and lubricants, and any foreign particles. The scoured braid is preferably stretched at a temperature between the glass transition temperature and melting temperature of the lower melting set of yarns. Therefore, the stretching temperature is such that none of the yarns is actually melted. The stretching operation densifies the braid and improves braid smoothness. Afterwards, the braid may be annealed while under restraint to improve dimensional stability, and in the case of absorbable braids, to improve the breaking strength retention in vivo.

If desired, the surface of the heterogeneous multifilament braid can be coated with a bioabsorbable or nonabsorbable coating to further improve the handleability and knot tiedown performance of the braid. For example, the braid can be immersed in a solution of a desired coating polymer in an organic solvent, and then dried to remove the solvent. Most preferably, the coating does not cause the fibers or yarns to adhere to one another increasing stiffness. However, if the surface of the heterogeneous braid is engineered to possess a significant fraction of the lubricous yarn system, the conventional coating may be eliminated saving expense as well as avoiding the associated braid stiffening.

If the surface of the braid is coated, than the coating composition may desirably contain bioactive materials such as antibiotics and growth factors.

The post-treated heterogeneous braid is sterilized so it can be used for a host of medical applications, especially for use as a surgical suture, preferably attached to a needle. The braid can be sterilized using any of the conventional techniques well known in the art. For example, sterilization can be effected by exposing the braid to gamma radiation from a cobalt 60 source. Alternatively, the braid can be sterilized by exposure to ethylene oxide.

In the following examples, the tensile properties and knot security are each determined using an Instron Tensile Tester. The tensile properties, i.e. the straight and knot tensile strength and the percent elongation, are determined generally according to the procedures described in U.S. Pat. No. 4,838,267. The knot security, which provides an indication as to the number of throws required to secure a knot so that it fails to slip before cleanly breaking, is measured by first tieing a conventional square knot around a mandrel, pulling the knot apart on the Instron Tester to observe whether slipping occurs, and if so, then tieing knots with additional throws until 20 out of 20 knots break cleanly without slipping. The bending rigidity, which is the inverse of pliability, is determined using a Kawabata Pure Bending Tester, as discussed in "The Effects of Structure on the Geometric and Bending Properties of Small Diameter Braids", Drexel University Master Thesis, 1991, by Mr. E. Ritter.

The examples are illustrative only, and are not intended to limit the scope of the claimed invention. The types of yarns used to prepare the heterogeneous braid and the yarn geometry can be varied to prepare heterogeneous braids within the scope of the claimed invention which exhibit a combination of outstanding physical or biological properties.

EXAMPLES

Examples I and II describe heterogeneous braids of PTFE and PET yarns. In order to evaluate the relative performance of these braids, two controls are included which represent 100% PET and 100% PTFE braids, respectively. To the extent possible, the yarn materials and processing conditions are identical for the controls and heterogeneous braid examples. In addition, for comparison purposes, a braid is fabricated with identical materials but processed per the prior art U.S. Pat. No. 4,470,941.

a) each yarn from the first set is composed of a plurality of filaments of a first fiber-forming material selected from the group consisting of PTFE, FEP, PFA, PVDF, PETFE, PP and PE; and

b) each yarn from the second set is composed of a plurality of filaments of a second fiber-forming material selected from the group consisting of PET, nylon and aramid; and

c) optionally a core.

2. The surgical suture of claim 1 wherein the suture is attached to a needle.

3. The surgical suture of claim 1 wherein the first fiber-forming material exhibits a surface energy less than about 38 dynes/cm.

4. The surgical suture of claim 3 wherein the first fiber-forming material exhibits a surface energy less than about 30 dynes/cm.

5. The surgical suture of claim 4 wherein the first set of yarns is PTFE.

6. The surgical suture of claim 5 wherein the second set of yarns exhibits a yarn tenacity greater than 3.0 grams/denier.

7. The surgical suture of claim 6 wherein the second set of yarns exhibits a yarn tenacity greater than 5.0 grams/denier.

8. The surgical suture of claim 1 wherein the second set of yarns is PET.

9. The surgical suture of claim 8 wherein the volume fraction of the first set of yarns in the braided sheath and core ranges from about 20 to about 80 percent.

10. The surgical suture of claim 9 wherein the fiber fineness of the yarns of the first and second sets is less than 10 denier per filament.

11. The surgical suture of claim 1 wherein at least one yarn from the first set of yarns is plied together to a yarn from the second set of yarns.

12. The surgical suture of claim 8 wherein the suture is attached to a needle.

* * * * *

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[redacted]

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Alastair Hunter et al.

Serial No.: Art Unit:

Filed : Examiner:

For : STERILIZED HETEROGENEOUS BRAIDS

#2

Hon. Commissioner of Patents
and Trademarks
Washington, D.C. 20231

INFORMATION DISCLOSURE STATEMENT

Dear Sir:

The following references are discussed in the Background of the Invention:

U.S. Patent 3,942,532 (Hunter, et al., issued March 9, 1976).

U.S. Patent 4,624,256 (Messier et al., issued November 25, 1986).

U.S. Patent 3,527,650 (Block, A., issued September 8, 1970).

U.S. Patent 4,470,941 (Kurtz, L., issued September 11, 1984).

WO 86/00020 (Kurtz et al., issued January 3, 1986).

The following additional references may be relevant to the examination of the above-identified application:

U.S. Patent 3,187,752 (Glick, A., issued June 8, 1965), discloses a tightly braided nonabsorbable suture coated with a polymeric silicone.

U.S. Patent 4,043,344 (Landi et al., issued August 23, 1977), discloses a nonabsorbable suture coated with a polyoxyethylene-polyoxypropylene copolymer.

VIA EXPRESS MAIL NO. HB346860118
MAILED FEBRUARY 19, 1992

U.S. Patent 4,047,533 (Periaccante et al., issued September 13, 1977), discloses an absorbable suture coated with a polyoxyethylene-polyoxypropylene copolymer.

U.S. Patent 4,946,467 (Ohi et al., issued August 7, 1990), discloses a suture having a core of one synthetic fiber material and a covering sheath of silk strands.

U.K. Patent Application GB 2 218 312A, discloses a fishing line of braided construction, some braid filaments being composed of polythene and other filaments composed of polyester and/or nylon.

German Patent DE 2949920, discloses a suture having a core of fibers composed of platinum or gold, and a braided sheath of fibers composed of polytetrafluoroethylene.

A completed Form PTO-1449 and a copy of each cited reference is attached herewith.

Respectfully submitted,

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February 19, 1992

United States Patent [19]
Hunter et al.

[11] 3,942,532
[45] Mar. 9, 1976

[54] BRAIDED SUTURE

[75] Inventors: Alastair Wilson Hunter; Darrell R. Thompson, both of Somerville, N.J.

[73] Assignee: Ethicon, Inc., Somerville, N.J.

[22] Filed: Aug. 15, 1974

[21] Appl. No.: 497,596

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 303,588, Nov. 3, 1972, abandoned.

[52] U.S. Cl. 128/335.5; 428/375
[51] Int. Cl.² A61L 17/00
[58] Field of Search ..... 128/335.5; 161/175, 176; 117/139.5 F, 161 R

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3,527,650	9/1970	Block	128/335.5 X
3,694,257	9/1972	Dumont	117/139.5 F
3,754,069	8/1973	Adams et al.	128/335.5 X
3,776,766	12/1973	Smerz et al.	117/139.5 F X
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Primary Examiner—Dalton L. Truluck
Attorney, Agent, or Firm—Wayne R. Eberhardt

[57] ABSTRACT

The tie-down characteristics of braided sutures are improved by applying to the surface thereof a polymeric ester of a dibasic acid and a glycol.

16 Claims, 3 Drawing Figures

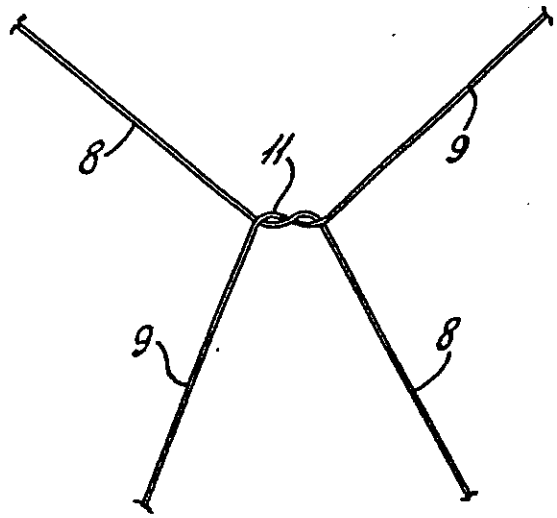


Fig. 1.

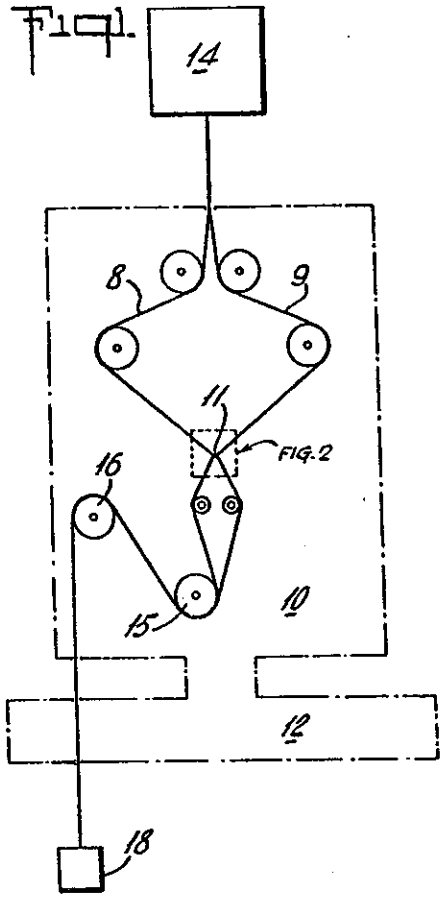


Fig. 2.

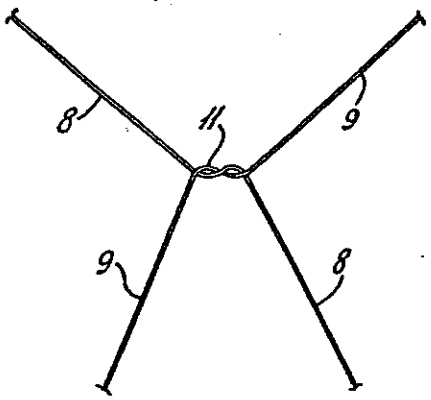
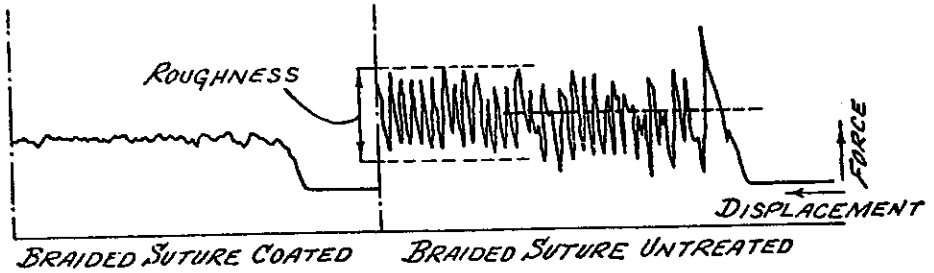


Fig. 3.



BRAIDED SUTURE

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of my co-pending U.S. application Ser. No. 303,588, filed Nov. 3, 1972 now abandoned.

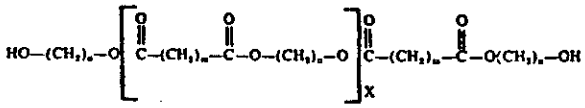
The present invention relates to surgical sutures and more specifically to multifilament sutures. Braided polyester multifilament sutures have been used by many surgeons for their strength and lack of tissue reactivity. Other surgeons prefer to use waxed silk when a non-absorbable suture is required because of its excellent hand, ease of knotting, and ease of passage through tissue.

An important characteristic of sutures in deep wound surgery is the ease of sliding a single throw knot down the suture into place. This behavior, sometimes referred to as the "tie-down performance" may be evaluated subjectively by tying a suture around a suitable mandrel. A single throw knot is formed and while pulling on the two free ends, the knot is forced to slide along the suture. The roughness or smoothness of this sliding action is an important criterion of performance.

Uncoated braids such as a braided polyethylene terephthalate suture give a very rough, jerky behavior while sutures coated with TEFLON, as described in U.S. Pat. No. 3,527,650 and wax-coated braided silk sutures are very smooth. Fortunately, the roughness or smoothness of tie-down can be measured and assigned a numerical value that will enable one to predict performance in the hands of the surgeon without reliance upon the subjective test referred to in the preceding paragraph. A method of using an INSTRON Universal Testing Instrument to determine tie-down performance is described below.

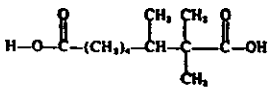
The present invention is directed to improving the tie-down characteristics of a braided suture by applying a surface coating of a non-toxic and physiologically inert polymer that does not adversely affect the hand or tensile properties of the suture.

It has now been discovered that the tie-down performance of braided, twisted, or covered multifilament sutures may be improved (the roughness decreased) by applying to the surface thereof polyesters derived from the polymerization of lactones or obtained by esterifying low molecular weight glycols with a dimeric acid. Preferred coating compositions are polyesters characterized by a melting point above room temperature and have the formula:

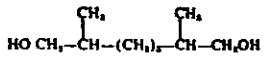


wherein n is an integer larger than 1 and smaller than 13, m is an integer larger than 1 and smaller than 9 and X is the degree of polymerization. Thus, stoichiometric quantities of succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic acid, or mixtures thereof may be condensed with ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, nonanediol, decanediol, undecanediol, dodecanediol, or mixtures thereof to obtain a polyester suitable for application as a surface coating. Polyesters of the above formula having a molecular weight in the range of approximately 1,000 to 15,000 and characterized by having at least two carbon atoms between the ester linkages in the polymer chain have been found to give the best lubricant and handling properties on silk and polyester sutures. Particularly preferred polyesters are those derived from 1,4-butanediol (n=4) and adipic acid (m=4) having a molecular weight of 2,000–3,000.

It will be understood that branched chain acids such as α,α,β-trimethylsuberic acid having the formula:

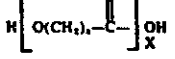


3,7-dimethyloctadienoic acid; 1,4-cyclohexanecarboxylic acid; mesatonic acid; β,β-dimethyl glutaric acid; and dimer acid; and branched chain diols such as diisononyl glycol having the formula:

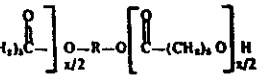


and glycols having a secondary hydroxyl group such as 1,2-propylene glycol may be added to the reaction mixture in small amounts as comonomers to produce polyesters suitable as coating materials that have a melting point above room temperature. The addition of larger amounts of such comonomers to the reaction mixture will result in low melting polyesters that are unsuitable for use in the present invention.

Polyesters that are useful in the manufacture of coated sutures in accordance with the present invention may also be prepared by polymerizing lactones. Such polyesters are characterized by a melting point above room temperature, and have the formula:



wherein n is an integer larger than 2 and X is the degree of polymerization. Particularly preferred is the polyester characterized by a molecular weight of about 2,000 obtained by polymerizing ϵ-caprolactones in the presence of a poly-methylenediol and having the formula:



wherein R is a polymethylene group derived from the poly-methylenediol and x is the degree of polymerization.

The polyester coating compositions described above are non-toxic and may be applied to the multifilament suture from solution. The multifilament suture may be

of braided, twisted, or covered construction. The construction of a covered suture is described in U.S. Pat. No. 3,791,388. The suture is then air dried to remove solvent and form a continuous surface coating.

The amount of the polyester coating composition applied to the suture may be varied depending upon the suture size and composition. Thus, the surface coating on a size 710 braided polyester suture may amount to from about 5 percent to as much as 7 percent of the weight of the suture. Sutures of larger size (size 5/0 – 5) require a smaller amount of the polyester coating composition (about 0.4 percent to 1 percent based upon the weight of the suture).

The surface coating composition (0.4 percent to about 7 percent based on suture weight) has no detrimental effect on tensile strength or stability. While the application of an excess of the surface coating composition has an effect on lubricity, it may detract from other physical properties of the suture, particularly knot stability.

A numerical value may be assigned to the tie-down performance of any braided suture when tested in accordance with the following procedure. In describing the test for tie-down performance reference is made to the accompanying drawings wherein:

FIG. 1 is a diagrammatic representation of an INSTRON Tester and shows two braided suture strands in position for testing;

FIG. 2 is an enlarged perspective view of the single throw knot illustrated in FIG. 1;

FIG. 3 is a reproduction of the tracing of an oscillographic recorder.

All tie-down measurements reported in the tables are made on a Table-Model INSTRON Tensile Tester using a Type B tension cell, full-scale range 100 to 2,000 grams. The INSTRON instrument is manufactured by the Instron Corporation of Canton, Massachusetts. A high-speed SANBORN Oscillographic Recorder (Model 7702A, manufactured by Hewlett-Packard, Waltham, Massachusetts) is substituted for the standard INSTRON Recorder which would be too slow to follow the rapid changes in force that result as the sutures under test slide against each other. A high-gain DC Amplifier (Hewlett-Packard Model 8803A, manufactured by Hewlett-Packard, Waltham Division, Waltham, Massachusetts) is used to interface this recorder with the INSTRON Transducer and a low-voltage DC power supply is provided to excite the transducer. The measurements are made in an air-conditioned laboratory at 72°F. and 50 percent relative humidity. To hold the specimen suture strands, a line contact jaw is used. The INSTRON machine is operated at a cross-head speed of 50 inches per minute and the chart speed of the oscillographic recorder is 20 millimeters per second.

Subjective tests for tie-down involved the suture configuration 11 shown in FIG. 2 (a single throw knot). The same configuration is produced by a pulley arrangement that is supported by a steel plate 10 shown in FIG. 1. The steel plate is attached to the cross-head 12 of the INSTRON Tester.

To perform tie-down measurements, two strands 8 and 9 of the same suture are attached at one end to the B cell transducer 14 of an INSTRON Tester. The sutures are threaded through the pulley arrangement as shown in FIGS. 1 and 2. The other end of the suture strands are brought together, passed around the pulleys 15 and 16, and attached together to a weight 18 which provides tension similar to that applied in a subjective test. A weight of 2.5 pounds is used in the standard procedure.

FIG. 3 shows actual recorder traces for a braided polyethylene terephthalate suture before and after coating with a polymer to improve tie-down performance. The roughness values are measured along the ordinate and throughout the specification and examples are recorded in pounds (roughness). When relatively smooth samples are compared, the amplitude of the oscillographic recorder can be increased by a factor of 20.

The present invention will be further illustrated by the following examples which illustrate preferred embodiments of the inventive idea.

EXAMPLE I

A condensation polymer is prepared by reacting 42.5 weight percent of 1,4-butanediol with 57.5 weight percent of adipic acid. The polymer so obtained is a firm, waxy solid having a viscosity of 1475 cps. at 60°C., a molecular weight of 2150, an acid number of 1.7, and a hydroxyl number of 52.1.

The polyester prepared as described in the preceding paragraph (4.84 parts by weight) is dissolved in 95.16 parts by weight of toluene and the solution is applied to a braided, size 2/0 polyethylene terephthalate suture strand using an ATLAB Yarn Finish Applicator manufactured by Precision Machine & Development Company, P.O. Box 645, New Castle, Delaware. The braid is coated under the following conditions:

Speed of Yarn	30 feet per minute
Hypodermic Syringe Size	30 cc.
Motor Drive Rate	10 r.p.m.
Hysteresis Tension	5 pounds.

The coated, braided strand is dried in forced air at 70°–80°F. to evaporate the solvent and is then collected on a take-up drum. No curing of the adipic ester is required. The coating is continuous over the entire surface of the suture and amounts to 1 percent by weight (based on the weight of the untreated suture). The coated braid is sterilized by exposure to cobalt-60 irradiation without significant loss of straight tensile strength or knot strength. The physical characteristics of the braided polyethylene terephthalate suture before and after coating are summarized in Table I.

TABLE I

	Braided Size 2/0 Polyethylene Terephthalate Suture (Untreated)	Braided Size 2/0 Polyethylene Terephthalate Suture (Coated)
Tensile Strength		
Non-Sterile	100,200 p.s.i.	99,100 p.s.i.
Sterile	99,400 p.s.i.	98,800 p.s.i.
Knot Strength		
Non-Sterile	53,900 p.s.i.	53,500 p.s.i.
Sterile	52,100 p.s.i.	55,000 p.s.i.

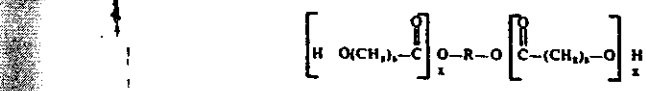
TABLE 1-continued

	Braided Size 2/0 Polyethylene Terephthalate Suture (Untreated)	Braided Size 2/0 Polyethylene Terephthalate Suture (Coated)
Roughness	3.67 lbs.	0.31 lbs.

Similar results are obtained when the polyester resin described in this Example is used to coat braided silk, cotton, and collagen sutures. However, higher levels of coating solids should be used for the hydrophilic substrates such as cotton and silk. The coated sutures made according to this example have excellent knot holding properties.

EXAMPLE II

A linear polymer of ϵ-caprolactone characterized by an average molecular weight of about 2,000 and having the structural formula:



wherein R is a polymethylene group derived from a polymethylenediol and x represents the degree of polymerization, was purchased from the Union Carbide Corporation, Chemical Division, 270 Park Avenue, New York City, New York. This polycaprolactone has a molecular weight of about 2,000 and is sold under the trade name NIAX POLYOL D-560.

The polycaprolactone identified above was dissolved in toluene to obtain a 3.8 percent by weight solution. This solution is applied to a braided, size 2/0 polyethylene terephthalate suture strand using an ATLAB Yarn Finish Applicator. The braid is coated under the conditions as described in Example I above and dried in forced air at 75°F. The coated braid, after evaporation of the solvent is collected on a take-up drum. No curing of the polycaprolactone is required. The coating is continuous over the entire surface of the suture and amounts to 1 percent by weight (based on the weight of the untreated suture). The coated braid is sterilized by exposure to cobalt-60 irradiation without appreciable loss of straight tensile strength or knot strength. The physical characteristics of the braided polyethylene terephthalate suture before and after coating are summarized in Table 2.

TABLE 2

	Braided Size 2/0 Polyethylene Terephthalate Suture (Untreated)	Braided Size 2/0 Polyethylene Terephthalate Suture (Coated)
Tensile Strength		
Non-Sterile	96,300 p.s.i.	92,000 p.s.i.
Sterile	95,100 p.s.i.	91,500 p.s.i.
Knot Strength		
Non-Sterile	53,900 p.s.i.	51,700 p.s.i.
Sterile	54,700 p.s.i.	51,700 p.s.i.
Roughness	2.77 lbs.	0.67 lbs.

Similar results are obtained when the polycaprolactone is used to coat braided silk, cotton, and collagen sutures of size 2/0 through 6/0. The polyesters of the present invention may also be used to coat absorbable synthetic sutures such as those described in U.S. Pat. No. 3,297,033 and 3,636,956 with a resulting improvement in tie-down characteristics.

What is claimed is:

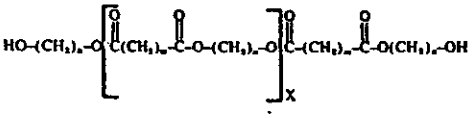
1. A suture having improved tie-down performance comprising a multifilament, the outer surface of the multiflament being coated with from about 0.4 percent to about 7 percent based on suture weight of an aliphatic polyester that is a solid at room temperature; said polyester having from 2 carbon atoms to about 12 carbon atoms between the ester linkages in the polymer chain and said polyester having a molecular weight in the range of 1,000 to 15,000.

2. The suture of claim 1, characterized by a braided construction.

3. The suture of claim 1, characterized by a twisted construction.

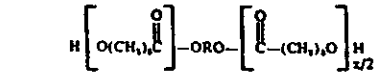
4. The suture of claim 1, characterized by a covered construction.

5. The multifilament suture of claim 1, wherein the polyester has the formula:



wherein *n* is an integer larger than 1 and smaller than 13, *m* is an integer larger than 1 and smaller than 9 and X is the degree of polymerization.

6. The multifilament suture of claim 1, wherein the polyester has the formula:



wherein R is a polymethylene group and X represents the degree of polymerization.

7. The multifilament suture of claim 1, wherein the polyester is a condensate of adipic acid and 1,4-butanediol having a molecular weight of about 2,000–3,000.

8. The suture of claim 7, wherein said multifilament is a silk multifilament and the polyester coating

amounts to about 5 p. ..nt of the weight of the untreated suture.

9. The suture of claim 7, wherein said multifilament is a polyethylene terephthalate multifilament, and the polyester coating amounts to about 1 percent of the weight of the untreated suture.

10. The multifilament suture of cliam 6, wherein the polyester coating has a molecular weight of about 2,000.

11. The suture of claim 10, wherein said multifilament is a polyethylene terephthalate multifilament and the polyester coating amounts to about 1 percent of the weight of the untreated suture.

12. The su...e of claim 10, wherein said multifilament is a silk multifilament and the polyester coating amounts to about 5 percent of the weight of the untreated suture.

13. The multifilament suture of claim 1, characterized by a roughness of less than 1 pound.

14. The multifilament suture of claim 2, characterized by a roughness of less than 1 pound.

15. The multifilament suture of claim 3, characterized by a roughness of less than 1 pound.

16. The multifilament suture of claim 4, characterized by a roughness of less than 1 pound.

* * * * *

United States Patent [19]
Messier et al.

[11] **Patent Number: 4,624,256**
[45] **Date of Patent: Nov. 25, 1986**

[54] **CAPROLACTONE POLYMERS FOR SUTURE COATINGS**

[75] Inventors: **Kenneth A. Messier**, Jewett City; **Joseph D. Kiss**, Old Lyme, both of Conn.

[73] Assignee: **Pfizer Hospital Products Group, Inc.**, New York, N.Y.

[21] Appl. No.: 774,636

[22] Filed: Sep. 11, 1985

[51] Int. Cl.⁴ A61L 17/00
[52] U.S. Cl. 128/335.5
[58] Field of Search 132/335.5

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Primary Examiner—Gregory E. McNeill
Attorney, Agent, or Firm—Charles J. Knuth; Peter C. Richardson; Gezina Holtrust

[57] **ABSTRACT**

High molecular weight caprolactone polymers are coated on surgical sutures to improve suture properties such as smooth surface, single knot slipdown, two throw knot slipdown for repositioning, and three throw knot security.

8 Claims, No Drawings

CAPROLACTONE POLYMERS FOR SUTURE COATING

BACKGROUND OF THE INVENTION

The invention relates to surgical sutures comprising a braided multifilament of a biocompatible material coated with a lubricating agent. More particularly, the invention relates to sutures coated with high molecular weight polycaprolactone or a high molecular weight copolymer of at least 90% by weight of caprolactone.

Coating of braided sutures with lubricating agents to improve knot slipdown properties is known in the art. For instance, U.S. Pat. No. 4,080,969 discloses coating braided polyglycolic acid filaments with diglycolate polyesters. U.S. Pat. No. 4,027,676 provides a coating for sutures comprising a bioabsorbable film-forming polymer, the bioabsorbable lubricant polyalkylene glycol and a hydrophobic material. U.S. Pat. No. 3,867,190 relates to polyglycolic acid sutures coated with a copolymer of lactic and glycolic acid. This patent also mentions incorporation of caprolactone in glycolide sutures. The formed copolymer contains not more than 15% by weight of caprolactone. Use of such copolymer in coating of sutures is not suggested.

U.S. Pat. No. 3,942,532 describes polyester multifilament sutures coated with polycaprolactone Niax Polyol D-560 having a low molecular weight of about 2,000 and a melt viscosity at 60° C. of 500 centipoise.

It is an object of the invention to provide a suture having a smooth surface, good single knot slipdown, two throw knot slipdown for repositioning, and three throw knot security.

SUMMARY OF THE INVENTION

In accordance with the invention, there is provided a surgical suture of a braided multifilament biocompatible, bioabsorbable material coated with a lubricating agent selected from the group consisting of high molecular weight polycaprolactone, a high molecular weight copolymer derived from at least 90% by weight of caprolactone and the remainder another biodegradable monomer, and a blend of at least 50% by weight of said polycaprolactone or said copolymer and up to 50% by weight of another biodegradable lubricating agent, based on the combined weights of the lubricating agents. The homopolymer or copolymer of caprolactone has a melt viscosity at 60° C. of at least about 50,000 centipoise (cps) or is a solid.

Generally, the lubricating agent or agents are present in an amount of about 0.5 to 10% by weight based on the suture.

The invention also provides for a needled surgical suture wherein a novel coated suture as described above is threaded through or fitted with a surgical needle, and a surgical suture package comprising a sterile enclosure containing a sterile needled coated surgical suture as previously described.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention, any conventional bioabsorbable suture material may be used. Sutures must be biocompatible such that they do not cause any adverse reactions in living tissue. The sutures of the invention are bioabsorbable such that they are slowly absorbed in living tissue. Examples of suitable bioabsorbable suture materials are collagen, poly(glycolic acid), poly(lactic acid), poly(hydroxybutyric acid), chitosan, chitin, carboxymethylcellulose etc. Preferably, the suture is made of poly(glycolic acid) or a glycolic acid copolymer containing at least 85% glycolic acid units.

The primary lubricating agent of the invention is high molecular weight polycaprolactone or a high molecular weight copolymer of at least 90% by weight of caprolactone and at most 10% by weight of another biodegradable monomer. Examples of such biodegradable monomers are glycolic acid, a glycolide, lactic acid, a lactide, p-dioxanone, valerolactone and other lactones derived from linear aliphatic hydroxycarboxylic acids, α-hydroxybutyric acid, ethylene carbonate, ethylene oxide, propylene oxide, propylene carbonate, malic acid ester lactones, succinic acid, adipic acid and other linear aliphatic dicarboxylic acids, and linear aliphatic diols such as butanediol and hexanediol.

High molecular weight polycaprolactone may be made by conventional methods for the polymerization of ε-caprolactone. Suitable polycaprolactones are commercially available, e.g. PCL-300 and PCL-700 of Union Carbide Corporation, also known by the brand names Tone P-300 and Tone P-700, respectively, having weight average molecular weights of about 15,000 and about 40,000, respectively, as reported by the manufacturer. Copolymers of caprolactone and another monomer may be made by conventional polymerization techniques, e.g. as described in U.S. Pat. No. 4,190,720.

When reference is made hereafter to polycaprolactone, this will include the above-described copolymers of caprolactone containing 10% or less of a biodegradable comonomer.

The high molecular weight polycaprolactone is applied to the multifilament suture generally from a solution in a solvent for polycaprolactone such as methylene chloride. Other known solvents for polycaprolactone may be used such as carbon tetrachloride, chloroform, ethyl acetate, cyclohexanone, methyl ethyl ketone, toluene, and xylene. The concentration of the polycaprolactone in the solvent may range from 1 to 10% by weight based on the solvent. Generally, about 5 g commercially available polycaprolactone per 100 ml of solvent is used. The preferred concentration will provide a readily flowable composition the solvent of which is not difficult to evaporate after the coating is applied, and will deposit the desired amount of polycaprolactone on the suture.

The sutures are immersed in the coating solution for 0.1 to 10 minutes, preferably about 0.2–3 minutes, and air dried at room temperature or, if desired, at slightly higher temperatures. The immersion may be carried out by batch dipping a skein or by continuously passing a continuous length of yarn through the coating solution.

The primary lubricating agent, high molecular weight polycaprolactone, may be mixed with other lubricating agents in an amount of up to 50% by weight of the combined lubricating agents. Examples of such other lubricating agents are poly(ethylene oxide), partially oxidized polyethylene wax, N,N'-ethylene diamine bis-stearamide, C_{10}–C_{30} fatty acid esters of sterols such as cholesterol and lanosterol, and polyalkylene glycols such as a copolymer of ethylene glycol and propylene glycol.

The coating composition may also contain other components for other purposes including dyes, stabilizers against oxidation or degradation caused by radiation, antibiotics, antiseptics, analgesics, anesthetics, anti-

inflammatory agents, growth or healing promoting agents and other pharmaceutically active ingredients.

Polycaprolactone is known to be a non-toxic material that degrades slowly in living tissue to form an innocuous metabolizable intermediate.

The following examples illustrate the invention. Examples 1–15 and 20 are comparative examples and Examples 16–19 are examples according to the invention.

EXAMPLES 1–19

Uncoated sutures of polyglycolic acid (18 inch long) were immersed in 100 ml of coating solution. The solvent, percentage by weight of coating material in solution, percentage coating by weight on the coated suture, and the size of the sutures are listed in Table 1.

The sutures were immersed in the coating solution for 2 to 3 minutes and air dried at room temperature. The percentage coating was calculated by weighing the suture on an analytical balance before and after coating and is given in Table I as percent of total weight of the coated suture. After air drying, the coated sutures were stored in a desiccator.

TABLE 1

Example	Suture size	Coating material	Solvent	% Coating material in solvent	% Coating on suture
1	2-0	PEO 8000	CH_2Cl_2	3	1.4
2	2-0	PGA powder	CH_2Cl_2	5	1.3
3	2-0	PEO 8000-PGA powder (5:1)	CH_2Cl_2	3.5	1.5
4	2-0	Pluracol P-4010	$CHCl_3$	3	1.0
5	3-0	PVP	$CHCl_3$	2	6.9
6	3-0	PVP	$CHCl_3$	2	1.7
7	3-0	PVA	H_2O	3	6.5
8	3-0	PEO 8000-calcium stearate (2:1)	CH_2Cl_2	3	3.4
9	2-0	Petrac 15	$CHCl_3$	5	3.5
10	2-0	Petrac 165	$CHCl_3$	5	2.9
11	2-0	PEG-100 stearate	CH_2Cl_2	5	4.4
12	2-0	PEG-40 stearate	CH_2Cl_2	5	3.9
13	2-0	Carnauba wax	$CHCl_3$	5	3.9
14	2-0	Kemamide W-40	$CHCl_3$	5	2.3
15	4-0	Cholesteryl palmitate	$CHCl_3$	5	2.5
16	1-0	PCL (Tone P300)	CH_2Cl_2	5	5.7
17	1-0	PCL (Tone P700)	CH_2Cl_2	5	6.1
18	1-0	PCL (Tone P700) Super Sterol Ester (1:1)	CH_2Cl_2	5	2.4
19	1-0	PCL (Tone P700) Super Sterol Ester (4:1)	CH_2Cl_2	5	3.1

The abbreviations and trademarks in Table I stand for the following:
PEO: poly(ethylene oxide)
PGA: poly(glycolic acid)
Pluracol P-4010: poly(propylene glycol)
PVA: poly(vinyl pyrrolidone)
Petrac 165: wax
Petrac 215: partially oxidized polyethylene wax (Petrochemicals Company Inc.)
PEG: poly(ethylene glycol)
Kemamide: N,N'—ethylene diamine bis-stearamide
PCL: polycaprolactone
Super Sterol Ester: cholesterol and lanosterol esters of a mixture of C_{10}—C_{30} fatty acids esters, supplied by CRODA Inc.

The melt viscosity of PCL (Tone P300) was measured with a Brookfield RVT viscometer having a No. 7 spindle at 20 and 50 rpm. The polymer was melted in a beaker and surrounded by a temperature controlled water bath, the temperature of which was measured with an electronic thermometer sensitive to ±0.1° C. The viscosity was 51,200 cps at 60° C. PCL (Tone P700)) is solid at 60° C. The molecular weight of PCL (Tone P700) was determined by gel permeation chromatography and was found to be 100,000 (polystyrene equivalent in dichloromethane).

Table 2 sets out the properties of the coated sutures of Table 1.

The general texture and feel of a suture such as flexibility, smoothness and hardness was observed by handling the suture and drawing between fingers. Typical observations as set out in Table 2 are stiff, silky, waxy.

The slipdown property of a suture was determined by tieing tightly a two-throw square knot, then grasping the long ears and pulling apart. If the suture was drawn through the knot, giving the appearance of the knot slipping down the braid, it was marked as excellent (exc.), good, or acceptable (acc.) depending on the ease of slipdown. If the knot seized or was difficult to slip down, the suture was marked as locks, poor, or rachety, depending on the difficulty of slip down.

The slipdown property was also tested under wet conditions by immersion of the unknotted suture in water for 5 seconds and immediately testing thereafter.

The knot security of a suture was tested by tying firmly a triple throw square knot and pulling the suture from a patient's side until the knot slipped or the suture broke. If the knot slipped, knot security was marked poor. If the suture broke without slip, the knot was sufficient to hold the suture at the knot and was marked acceptable in Table 2.

The knot security was tested under wet conditions by immersion of the unknotted suture in water for 5 seconds and immediately testing thereafter.

The wet knot slipdown was tested by tieing tightly a two-throw granny knot and slipping down the knot. The knot was then wetted by rubbing with fingers dipped in water. An attempt was then made to slip the knot down further. If the knot slipped both dry and wet, the suture was marked as acceptable, good, or excellent depending on the ease of the slip. If the knot slipped dry but not wet, the suture was marked as locking. If the slip was poor wet and dry and locking was difficult to determine, the suture was marked poor, or rachety.

TABLE 2

Example	Texture	2 throw square slipdown dry	2 throw square slipdown wet	3 throw square slipdown dry	3 throw square slipdown wet	2 throw granny slip-down, wet knot	Comments
1	stiff	exc.	poor	acc.	acc.	locks	exc. dry, poor wet
2	powdery smooth	poor	locks	acc.	acc.	locks	poor lubr. overall
3	stiff	exc.	poor	acc.	acc.	locks	exc. dry, poor wet
4	silky	acc.	acc.	acc.	acc.	locks	acc. lubr. but locks
5	very stiff	poor	locks	acc.	acc.	locks	very poor lubr., locks
6	very stiff	locks	locks	acc.	acc.	locks	as 5
7	stiff, rough	rach-ety	locks	acc	acc.	poor	poor lubr. esp. wet
8	silky	exc.	poor, rachety	acc.	acc.	locks	exc. slip-down dry, but rvw when wet

TABLE 2-continued

Example	Texture	2 throw square slipdown dry	2 throw square slipdown wet	3 throw square slipdown dry	3 throw square slipdown wet	2 throw granny slip-down, wet knot	Comments
9	stiff, rough	exc.	exc.	acc.	acc.	exc., no locking	excellent
10	very rough	rach-ety	rachety	acc.	acc.	rachety	poor lubr., not affected by water
11	stiff, waxy	very good	good	acc.	acc.	rachety	fairly good, not much affected by water
12	stiff, smooth	rach-ety	rachety	acc.	acc.	rachety	poor lubr., not affected by water
13	rough	fine to rach-ety	good	acc.	acc.	acc.	rachety dry, good wet
14	waxy, rough	good	good	acc.	acc.	good	good, not affected by water
15	rough	poor	poor	acc.	acc.	poor	poor lubr. overall
16	stiff, waxy	exc.	exc.	acc.	acc.	exc.	as 14
17	stiff, waxy	exc.	exc.	acc.	acc.	exc.	as 14
18	silky, good feel	exc.	exc.	acc.	acc.	exc.	exc. good feel, good lubr., not affected by water
19	stiff	exc.	exc.	acc.	acc.	exc.	as 18.

"lubr.": lubricant

COMPARATIVE EXAMPLE 20

An uncoated suture of polyglycolic acid (54 inch long), size 3-0 was immersed in 100 ml of coating solution comprising 95.0 ml methylene chloride and 5.00 g of Tone polyester 0240 (formerly Niax Polyol D560) of Union Carbide Corporation. The manufacturer specifies a molecular weight of 2000 and a viscosity of 500 cps at 60° C. for Tone polyester 0240. The coating solution was obtained by dissolving the Tone polyester 0240 at room temperature in a 200 ml beaker in 3 minutes using a magnetic stirrer.

The suture was immersed in the coating solution for one minute and air-dried at room temperature. The % coating on the suture was 5.9.

Knot slip and knot security were determined as follows.

Knot	Result
2 throw square slip down	slips about 0.5 inch.
3 throw square slipdown	locks and breaks locks
2 throw granny slipdown (dry)	acceptable slip
2 throw granny slipdown (wet)	acceptable slip

I claim:

1. A surgical suture comprising a braided multifilament of poly(glycolic acid or a copolymer containing at least 85% glycolic acid units coated with a lubricating agent selected from the group consisting of a high molecular weight homopolymer of caprolactone, a high molecular weight copolymer of at least 90% by weight of caprolactone and the remainder another biodegradable monomer, and a blend of at least 50% by weight of said homopolymer of said copolymer of caprolactone and up to 50% by weight of another biodegradable lubricating agent, said homopolymer or copolymer of caprolactone having a melt viscosity at 60° C. of at least about 50,000 centipoise or being solid.

2. A suture according to claim 1 wherein said other biodegradable lubricating agent is a mixture of sterol esters of C_{10}–C_{30} fatty acids.

3. A suture according to claim 2 wherein said sterol is a mixture of cholesterol and lanosterol.

4. A suture according to claim 1 wherein said lubricating agent is present in an amount of 0.5 to 10% by weight based on the weight of the suture.

5. A needled surgical suture comprising at least one filament of poly(glycolic acid) or a copolymer containing at least 85% glycolic acid units coated with a lubricating agent selected from the group consisting of a high molecular weight homopolymer of caprolactone, a high molecular weight copolymer of at least 90% by weight of caprolactone and the remainder another biodegradable monomer, and a blend of at least 50% by weight of said homopolymer or said copolymer of caprolactone and up to 50% by weight of another biodegradable lubricating agent, said homopolymer or copolymer of caprolactone having a melt viscosity of 60° C. of at least about 50,000 centipoise.

6. A needled surgical suture according to claim 5 wherein said other biodegradable lubricating agent is a mixture of sterol esters of C_{10}–C_{30} fatty acids.

7. A surgical suture package comprising a sterile enclosure containing a sterile needled surgical suture, the suture comprising at least one filament of poly(glycolicacid) or a copolymer containing at least 85% glycolic acid units coated with a lubricating agent selected from the group consisting of a high molecular weight homopolymer of caprolactone, a high molecular weight copolymer of at least 90% by weight of caprolactone and the remainder another biodegradable monomer, and a blend of at least 50% by weight of said homopolymer of said copolymer of caprolactone and up to 50% by weight of another biodegradable lubricating agent, said homopolymer or copolymer of caprolactone having a melt viscosity at 60° C. of at least about 50,000 centipoise or being solid.

8. A package according to claim 7 wherein said other biodegradable lubricating agent is a mixture of sterol esters of C_{10}–C_{30} fatty acids.

* * * * *

United States Patent Office 3,527,650 Patented Sept. 8, 1970

3,527,650

SUTURE COATING OF POLYETHYLENE OR POLYTETRAFLUOROETHYLENE

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Int. Cl. A61l 17/00
U.S. Cl. 117—7 8 Claims

ABSTRACT OF THE DISCLOSURE

The hand and lubricity of a braided polyethylene terephthalate suture are improved by applying to the surface thereof polymers of polyethylene or polytetrafluoroethylene having a lower coefficient of friction than the suture and a styrene-acrylic ester copolymer resin binder therefor.

The present invention relates to nonabsorbable surgical sutures and more specifically to braided multifilament sutures of polyethylene terephthalate. Braided polyethylene terephthalate sutures have been used by many in the surgical profession for years and actually are preferred over silk by many surgeons for their strength and lack of tissue reactivity. Other surgeons prefer to use waxed silk when a nonabsorbable suture is required because of its excellent hand, ease of knotting, and ease of passage through tissue.

It is a known disadvantage of polyethylene terephthalate sutures that the knot may slip unless repeated knots are tied. Attempts have been made to improve the knotability of polyethylene terephthalate by modifying the surface thereof to decrease lubricity. One method of doing this is described in U.S. Pat. No. 3,307,971, which issued to Leonard D. Kurtz in March of 1967.

The present invention is directed to increasing the lubricity of a braided polyethylene terephthalate suture by applying a surface coating of a nontoxic and physiological inert resin that has a lower coefficient of friction than the polyethylene terephthalate, such as, polytetrafluoroethylene or polyethylene.

Polytetrafluoroethylene has been applied to braided polyethylene terephthalate sutures for the purpose of filling the interstices of the braided structure and achieving the characteristics of a solid monofilament. U.S. Pat. No. 3,322,125 described in Example I impregnating a braided 4/0 polyethylene terephthalate suture with a suspension of polytetrafluoroethylene particles having a particle size of about 0.2 micron. The suture is dried and stretched at 450° F. whereby the particles of polytetrafluoroethylene are trapped within the body of the suture.

The process described in U.S. Pat. No. 3,322,125, however, does not produce a satisfactory surface coating of polytetrafluoroethylene because the polytetrafluoroethylene particles do not adhere to the surface of the suture material. The particles can flake off and produce foreign body reactions near the suture site. It has now been discovered that polytetrafluoroethylene and other resinous particles having a coefficient of friction lower than that of the braided polyethylene terephthalate surface may be cemented to the surface of the braided polyethylene terephthalate suture with a binder resin which prevents flaking of the resinous particles.

Binder resins that are suitable for use in securing polytetrafluoroethylene and similar resinous particles having a lower coefficient of friction than polyethylene terephthalate to the surface of a braided polyethylene terephthalate suture are the non-ionic, self-cross linking, or cross-linkable acrylic polymers, such as Rhoplex HA–12 and Rhoplex B–15, manufactured by Rohm and Haas Company, Philadelphia, Pa., and thermoplastic acrylic

polymers, such as Hycar 2601, manufactured by B. F. Goodrich Chemical Company of Cleveland, Ohio and copolymers of an acrylic ester and styrene, such as Aerotex Resin 134, manufactured by the American Cyanamid Company, Bound Brook, N.J.

In the practice of the present invention, a braided polyethylene terephthalate suture is passed through an aqueous mixed dispersion of an acrylic latex of the type identified above and polytetrafluoroethylene particles or polyethylene particles. The ratio of acrylic latex to polytetrafluoroethylene particles in the dispersion is about 1:3 but may be increased to improve the adhesion of the lubricating particles to the surface of the suture or decreased to increase the lubricity of the surface coating. The dwell time of the braided suture with the polytetrafluoroethylene dispersion is just sufficient to coat the surface as penetration of the lubricant particles into the interstices of the suture is not necessary or desired. The braided polyethylene terephthalate after it leaves the coating bath is dried and heat cured. The structure of the braided polyethylene terephthalate suture is altered by the shrinkage that occurs during the curing process. To restore the original close braided structure and control the size (diameter), the coated, braided suture after cooling is heated and stretched under tension. The coated, braided strand may be conveniently heated by moving it one or more times past a steel plate maintained at a temperature between 350° F. and about 440° F. at the rate of 50 to 100 yards per minute. The smaller size sutures, e.g., size 6/0, may be stretched in this manner about 25 percent to 40 percent. The larger sutures, e.g., size 2, are stretched as as much as 40 percent to 60 percent.

It is an important aspect of the present invention that the binder resin is flexible and bound to the braided suture in such a manner that it does not crack, flake, or come off of the suture during the heat-stretching step.

The product so obtained has an improved hand and surface lubricity. Yet the knot will not slip if a double square knot is tied. The surface lubricity of a coated polyethylene terephthalate suture may be demonstrated by the following test:

To the cross bar of an Instron tester is secured a 3½" pulley and a 2" pulley. Using a B cell and the associated upper jaw (red), the instrument is calibrated with a 100 gram weight on the B cell clamp to full scale deflection on the ×1 scale.

To determine the surface lubricity of a coated strand, a 45" length of suture is clamped in the center of the upper jaw; the free end is passed counterclockwise around the 3½" diameter pulley, and a counterclockwise single throw is made approximately 1½" above the face of the 3½" diameter pulley wheel. The free end of the suture is then passed over the 2" diameter pulley wheel and secured to a 50 gram weight. The distance from the periphery of the pulley face to the bottom of the B cell clamp is 2½".

In operation, the ×10 scale on the Instron tester is used (1,000 grams full scale) and the crosshead speed and chart speed are 20" per minute.

As the suture passes over itself, a curve is plotted on the graph paper. Since a braided suture has braid protrusions and is somewhat elliptical in cross-section, a smooth curve does not appear. The "stick" portion of a stick-slip curve is produced when it is easier for the suture to stick to itself and elongate than to slip. As the suture is elongated more and more, the tension continues to build up until either the yield point of the suture is reached or until the cohesive force is overcome and the suture slips. This cycle is repeated producing a saw-tooth pattern on the chart.

The surface lubricity of the braided suture may be determined from the maximum and minimum friction

peaks on the graph in accordance with the following equation:

$$\text{average lubricity} = \text{minimum peak} + \frac{(\text{maximum peak} - \text{minimum peak})}{2}$$

The lubricity of the surface as determined by the test described above may be confirmed subjectivly (by feel).

Microscopic examination of the surface coated braided sutures confirms that the surface coating does not scuff or flake off on tie-down.

The invention will be understood from the following examples which illustrate preferred embodiments of the inventive idea.

EXAMPLE I

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0[1], passed beneath two nylon rollers immersed in a trough containing a polytetrafluoroethylene resin dispersed in a thermosetting acrylic latex (Emralon 312, manufactured by Achesin Collids Company, Port Huron, Mich.). The polytetrafluoroethylene resin constitutes about 50 percent of the total resin solids. The braided multifilament moves through the trough at the rate of about 16 yards per minute, the surface of the skein being in contact with the liquid dispersion for about 0.6 to 0.9 seconds. The concentration of resin solids in the trough was maintained at 50±5 percent throughout the run.

After coating, the skein is heated in an over for ½ hour at 300° F. and heat stretched 40 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 3 percent of the total suture weight.

The surface lubricity, as measured by the Instron surface lubricity test described above, is 500 grams. The coated suture does not slip when tied with a double square knot.

EXAMPLE II

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is coated by passing it though one foot in length that contains a resinous dispersion having the following composition:

	Parts
Acrylic resin 45 percent solids (Rhoplex HA-12)	707
Polytetrafluoroethylene resin 60 percent solids (Teflon 30 manufactured by E. I du Pont de Nemours and Company, Inc., Wilmington, Del.)	1,588
Water	7,705

The skein moves through the trough at a speed of 20 feet per minute and is heated in an oven for ½ hour at 300° F. and heat stretched 35 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 3.8 percent of the total suture weight. The surface lubricity, as measured by the Instron surface lubricity test described above, is 550 grams. The coated suture does not slip when tied with a double square knot.

EXAMPLE III

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is passed beneath two nylon rollers immersed in a trough containing 340 parts of a polytetrafluoroethylene resin containing 60 percent resin solids and 151 parts of a thermosetting acrylic latex

[1] Diameter 10–13 mils as determined by the method described at p. 918 of the U.S. Pharmacopeia, vol. XVII.

(45 percent solids). The acrylic latex is an interpolymer of 90 parts of 2-ethylhexyl acrylate, 12 parts glycidyl acrylate, 90 parts styrene, and 8 parts methacrylic acid. The braided multifilament moves through the trough at the rate of about 16 yards per minute, the surface of the skein being in contact with the liquid dispersion for about 0.6 to 0.9 second.

After coating, the skein was heated in an oven for ½ hour at 275° F. and heat stretched 45 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 2.6 percent of the total suture weight.

The surface lubricity, as measured by the Instron surface lubricity test described above, is 530 grams. The coated suture does not slip when tied with a double square knot.

EXAMPLE IV

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is coated by passing it through a trough one foot in length that contains a resinous dispersion having the following composition:

	Parts
Acrylic resin 46 percent solids (Rhoplex B-15)	832
Polytetrafluoroethylene resin 60 percent solids (Teflon 30)	1,868
Water	7,300

The skein moves through the trough at a speed of 20 feet per minute and is heated in an oven for ½ hour at 300° F. and heat stretched 50 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating. The surface lubricity, as measured by the Instron surface lubricity test described above, is 490 grams. The coated suture does not slip when tied with a double square knot.

EXAMPLE V

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is passed beneath two nylon rollers immersed in a trough containing 1,494 parts of a tetrafluoroethylene resin containing 60 percent resin solids (Teflon 30); 1,192 parts of a styrene acrylate copolymer resin latex (Aerotex Resin 134); and 7,314 parts of water. The braided multifilament moves through the trough at the rate of about 20 feet per minute.

After coating, the skein was heated in an oven for ½ hour at 300° F. and heat stretched 55 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 3.94 percent of the total suture weight.

The surface lubricity, as measured by the Instron surface lubricity test described above, is 466 grams. The coated suture does not slip when tied with a double square knot.

EXAMPLE VI

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is coated by passing it through a trough one foot in length that contains a resinous dispersion having the following composition:

	Parts
Polyethylene resin 50 percent solids Valsof K070 manufactured by Valchem Chemical Division of United Merchants and Manufacturers, Inc., New York, N.Y.	126
Acrylic resin (45 percent solids) (Rhoplex HA-12)	126
Water	748

The skein moves through the trough at a speed of 20 feet per minute and is heated in an oven for ½ hour at 300° F. and heat stretched 40 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 3.3 percent of the total suture weight. The dry straight tensile strength is 9.1 pounds, and the dry knot strength is 6.4 pounds. The coated suture does not slip when tied with a double square knot.

EXAMPLE VII

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is coated by passing it through a trough one foot in length that contains a resinous dispersion having the following composition:

	Parts
Polyethylene resin 30 percent solids Valspex N-123 manufactured by the Valchem Division of United Merchants and Manufacturers, Inc., New York, N.Y.	3,375
Non-crosslinking acrylic resin (Hycar 2601)	675
Water	5,950

The skein moves through the trough at a speed of 20 feet per minute and is heated in an oven for ½ hour at 300° F. and heat stretched 45 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating amounting to 3.5 percent of the total suture weight.

EXAMPLE VIII

A braided skein of polyethylene terephthalate (Dacron) multifilament, size 2/0, is coated by passing it through a trough one foot in length that contains a resinous dispersion having the following composition:

	Parts
Acrylic resin 50 percent solids (Hycar 2601)	720
Polytetrafluoroethylene resin 60 percent solids (Teflon 30)	1,868
Water	7,412

The skein moves through the trough at a speed of 20 feet per minute and is heated in an oven for ½ hour at 300° F. and heat stretched 40 percent by passing the moving skein 12 times under tension in close proximity to an 18-inch plate heated to 440° F.

The product so obtained has utility as a suture. It has an excellent hand and a smooth, resinous surface coating. The surface lubricity, as measured by the Instron surface lubricity test described above, is 553 grams. The coated suture does not slip when tied with a double square knot.

The invention described and illustrated herein before and secured by this Letters Patent is defined in the following patent claims.

What is claimed is:

1. A braided polyethylene terephthalate suture having a surface coating of a first resin selected from the group consisting of tetrafluoroethylene and polyethylene and a second binder resin comprising a styrene-acrylic ester copolymer, the weight ratio of said first resin to said second resin being between about 1:1 and about 3:1.

2. The suture of claim 1, wherein said first resin is polytetrafluoroethylene.

3. The suture of claim 1 wherein said acrylic ester copolymer is a copolymer of 2-ethylhexyl acrylate.

4. The suture of claim 1, wherein said first resin is polyethylene.

5. A method of improving the hand and surface lubricity of a braided polyethylene terephthalate suture comprising the steps of immersing the suture in an aqueous dispersion of a first resin selected from the group consisting of tetrafluoroethylene and polyethylene and a second binder resin comprising a styrene-acrylic ester copolymer, the weight ratio of said first resin to said second resin being between about 1:1 and about 3:1, for a time sufficient to wet the surface of said suture but not sufficient for said resins to substantially penetrate into the interstices of said suture, drying the suture, curing the binder resin, and heating and stretching the suture at an elevated temperature, whereby a resinous coating is formed on the surface of the suture.

6. The method of claim 5, wherein said first resin is polytetrafluoroethylene.

7. The method of claim 5, wherein said suture is heated at about 300° F. for about one-half hour.

8. The method of claim 5, wherein said first resin is polyethylene.

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